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By

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On the Equilibrium Silicide in Beta Ti-V Alloys Containing Si

by

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The addition of small amounts of silicon (usually less than ~1 at. pct.) to strengthen α(hcp)—β(bcc) and martensitic Ti alloys is well established. The equilibrium silicide formed in these alloys has been identified as hexagonal Ti_5Si_3[1,2] (or $(Ti,Zr)_5Si_3$ phase in alloys containing Zr),[1,3,4] although there is also a report of a tetragonal Ti_3Si phase.[5] The use of Si to age harden β Ti alloys, specifically Ti-V-Si alloys, has also been reported.[6-9] While the precipitation sequence in these alloys involves an identifiable hexagonal transition phase,[8,9] there is a question as to nature of the equilibrium silicide. Based on electron diffraction evidence, Godden[9] observed the formation of a hexagonal $(Ti,V)_5Si_3$ phase from the transition phase particles in β Ti-V-Si alloys; he concluded that the $(Ti,V)_5Si_3$ particles are the equilibrium phase. Working with high purity β Ti-V-Si alloy single crystals, Tuominen et al[8] did not observe any similar decomposition, and a hexagonal $(Ti,V)_5Si_3$ phase was not seen despite long aging times. The purpose of this communication is to provide both x-ray and electron diffraction evidence for the existence of a tetragonal silicide, most likely $(Ti,V)_3Si$ but conceivably of $(Ti,V)_5Si_3$. We conclude that this is an equilibrium phase in certain β-phase Ti-V alloys containing Si.

The specimens used for this study were arc-melted, homogenized at 1300°C for four hours and, after heat treating, had a composition of Ti-38-a/oV-1a/oSi (Ti-40w/oV-0.6w/oSi) with an interstitial content (in wt ppm) of: 600 O, 55 N,

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70 H, and 90 C. Thin foils were prepared by electropolishing in a 5% H_2SO_4-methanol solution cooled to -50°C and examined in a Philips EM301G. X-ray diffraction data were obtained from one-quarter inch diameter polished discs using a diffractometer incremented in 0.1° steps.

For specimens aged up to 256 hours at 570°C, the x-ray diffraction data yields interplanar spacings which cannot be indexed as a hexagonal $(Ti,V)_5Si_3$ silicide. However, all the interplanar spacings can be accounted for if the precipitate has a tetragonal crystal structure with lattice parameters a = 10.02 Å and c = 4.965 Å. This is shown in Table I with the experimental and calculated interplanar spacings agreeing reasonably well.

The tetragonal precipitates have a faceted appearance and tend to nucleate preferentially at grain boundaries, thus explaining the difficulty observing these particles in single crystals.[8] Figure 1 shows typical selected area electron diffraction patterns obtained by tilting the sample to excite both precipitate and matrix reflections. Similar diffraction patterns have been obtained from silicide precipitates in a Ti-30V-1Si alloy aged for long times at 570°C.[10] Analysis of these and other patterns yields interplanar spacings consistent with those determined by x-ray diffraction. Interplanar angles were measured and agree with the calculated angles to within one degree. There are no readily identifiable matrix-precipiate orientation relationships, although the faceted appearance indicates at least some degree of coherence.

The previously reported tetragonal Ti_3Si silicide phase has lattice parameters of a = 10.39 Å and c = 5.17 Å,[5] which are near those observed (a= 10.02 Å and c = 4.96_5 Å) especially when one notes that vanadium has a smaller size than that of titanium. Energy dispersive analysis by x-rays shows that the particles contain a substantial amount of silicon but the exact concentration could not be determined. We thus conclude that the observed particles are a tetragonal silicide, probably of the type "$(Ti,V)_3Si$" in agreement with Schubert et al.[5]

There are a number of reasons why the tetragonal phase appears to be the equilibrium silicide in this alloy. The observation that these particles cause a dissolution of the transition $(Ti,V)_xSi_y$ (see Fig. 7 of Ref. 8) indicates that the tetragonal silicide is more stable. The nucleation of "$(Ti,V)_3Si$" particles at grain boundaries is consistent with the nucleation of equilibrium phases in order to reduce their interfacial energy term.[11] No tetragonal silicides were seen after aging at 450°C in Ti-30V-1Si, which is compatible with the fact that such phases also have difficulty nucleating at low aging temperatures where the driving forces favor transition phases with small interfacial free energies.[10] Perhaps most important is the observation that aging times as long as 256 hrs at 570°C or 32 hours at 650°C did not produce any precipitate other than the "$(Ti,V)_3Si$" phase. These particles as well as the rod-like $(Ti,V)_xSi_y$ transition phase precipitates merely coarsen at long aging times in the Ti-38V-1Si alloy.

In contrast, Godden[9] observes the break-up of the transition phase $(Ti,V)_xSi_y$ rods into rows of cube-shaped, hexagonal $(Ti,V)_5Si_3$ particles with continued aging at the same range of temperatures in a Ti-45V-1Si alloy. Thus similar Ti-V-Si alloys yield different "equilibrium" silicides. In addition, the transformation sequence differs. In the higher V alloy, the transformation from the transition phase to the $(Ti,V)_5Si_3$ phase probably occurs directly and assumes a definite orientation relationship with the bcc matrix. In the present case, most of the "$(Ti,V)_3Si$" phase is confined to the grain boundaries and those few particles which nucleate intragranularly have no consistent matrix-particles orientation relationship.

We have no clear-cut explanation for the tetragonal "$(Ti,V)_3Si$" vs. the hexagonal $(Ti,V)_5Si_3$ observations, as both appear to be equilibrium phases. A comparison of the interstitial contents of our and Godden's Ti-V-Si alloys show similar oxygen and nitrogen contents, but somewhat less carbon (90 vs. 130 ppm) and more hydrogen (70 vs. 10 ppm) in our alloy than in Godden's.[9] It is well known that a number of tetragonal M_5Si_3 silicides (where M = Mo, Nb, V, Cr, W, or

Ta and, like Ti-38V, is bcc) undergo a transition to a hexagonal M_5Si_3 with the addition of carbon.[12] We further note that the lattice parameters of the tetragonal M_5Si_3 phases are similar in magnitude to that of the present silicide. Thus we speculate that a low carbon content and/or a difference in carbon distribution may be a factor in stabilizing the present tetragonal silicide, which conceivably could have a chemistry of $(Ti,V)_5Si_3$.

Summarizing, both x-ray and electron diffraction observations indicate the presence of a tetragonal silicide which we conclude is an equilibrium phase in Ti-30 to 40V-1Si alloys aged at $\sim$600°C. This silicide probably has a chemistry of $(Ti,V)_3Si$ but conceivably could be a tetragonal $(Ti,V)_5Si_3$ phase.

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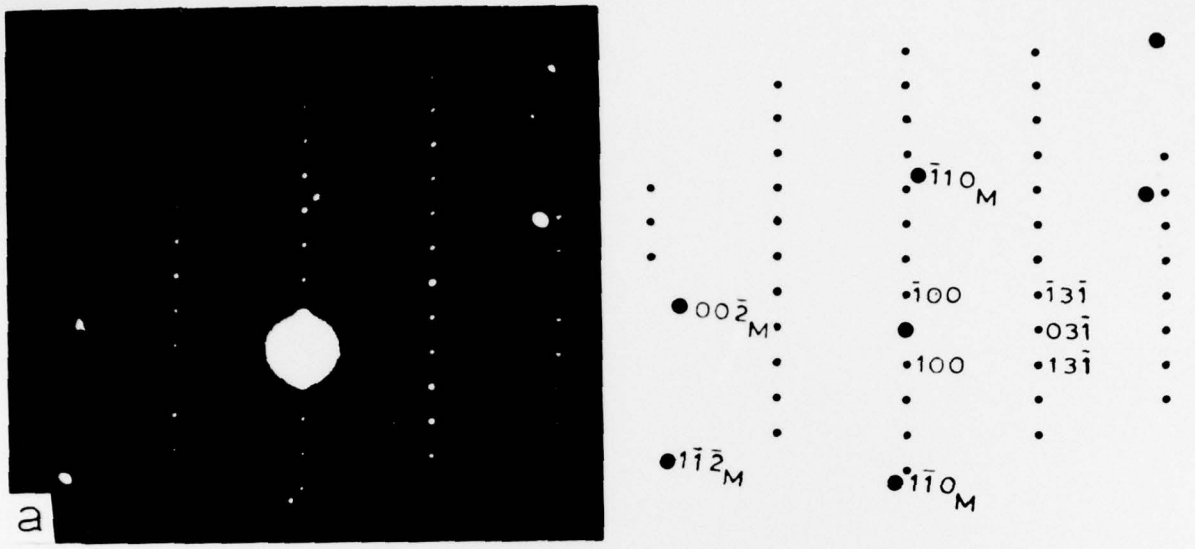
Table I

A Comparison of Observed and Calculated Interplanar Spacings of Silicide Precipitates in a Ti-38V-1Si Alloy, which was Quenched and Aged 128 Hours at 570°C.

Line	2θ	EXP. "d" Spacings Using CuK α Radiation (Å)	Assigned hkℓ	Calculated "d" Spacings (Å)*
1	12.40	7.14	110	7.09
2	17.90	4.96	200	5.01
3	19.90	4.46	210	4.48
4	24.90	3.58	220	3.54
5	26.50	3.36	211	3.33
6	28.60	3.12	310	3.17
7	30.60	2.92	221	2.88
8	34.10	2.63	311	2.67
9	36.00	2.49	002	2.48
10	37.80	2.38	330	2.36
11	38.50	2.34	112	2.34
12	42.70	2.12	331	2.13
13	44.60	2.03	222	2.03
14	52.50	1.74	412	1.74

* Using a = 10.02 Å, c = 4.965 Å.



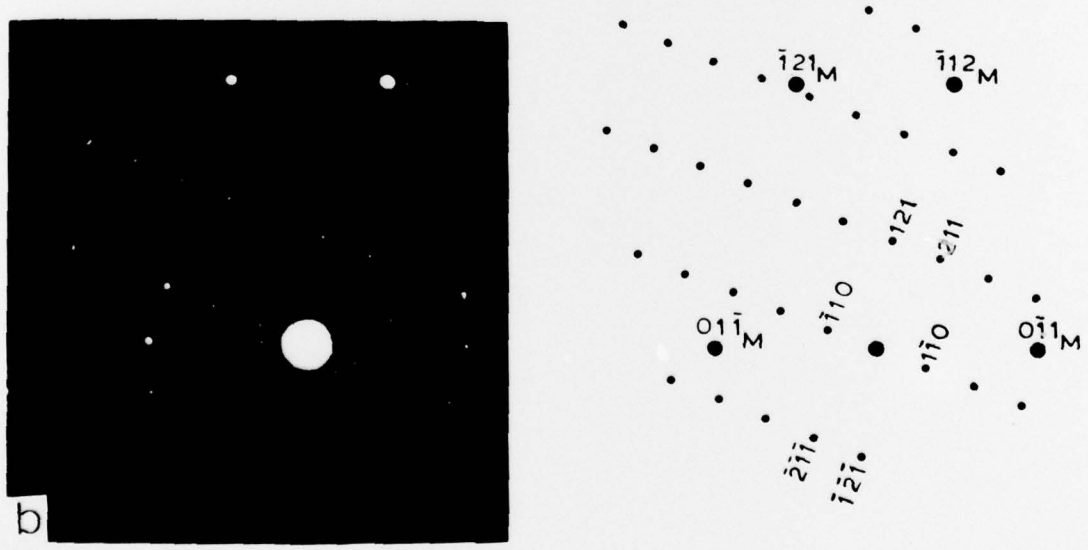


Figure 1. Selected area diffraction patterns of $(Ti,V)_3Si$ particles.
(a) $\langle 110 \rangle_M$, $(0\bar{1}3)$ precipitate reciprocal lattice plane.
(b) $\langle 311 \rangle_M$, $(\bar{1}\bar{1}3)$ precipitate reciprocal lattice plane.

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